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COMPUTED PROPERTIES OF 1,1-DIAMINO-2,2-DINITROETHYLENE

by

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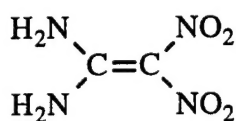
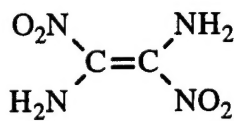
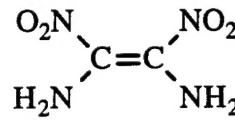
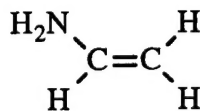
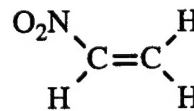
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### Introduction:

1,1-Diamino-2,2-dinitroethylene, **1**, is of interest as a potentially significant energetic compound. It has the same molecular stoichiometry as HMX and RDX, and accordingly the same high value for moles of gaseous products (CO, N<sub>2</sub> and H<sub>2</sub>O) per gram, 0.0405.

We have carried out a computational analysis of **1**, in order to provide data relevant to its potential energetic performance. These include: a) heats of formation (solid, liquid and gas phase), and heats of vaporization and sublimation; b) specific impulse; c) C–NO<sub>2</sub> and C–NH<sub>2</sub> bond strengths; and d) molecular geometry. In order to provide perspective in regard to the last point, we have also computed the geometries of the two isomers of **1** formed by interchanging NO<sub>2</sub> and NH<sub>2</sub> groups, **2** and **3**, as well as the two monosubstituted ethylenes, **4** and **5**.

**1****2****3****4****5**

### Heats of formation:

We have used our density functional procedure [1] to compute the gas phase heat of formation of **1**. The vibrational energy was determined from the molecular stoichiometry [2]. The gas phase heat of formation is converted to the liquid and solid state values by subtracting, respectively, the heat of vaporization and the heat of sublimation. These are obtained by means of relationships that we have developed involving the computed electrostatic potential on the molecular surface [3,4].

### Results:

$$\Delta H_f^{298K}(\text{gas}) = -1.2 \text{ kcal/mole} = -7.8 \text{ cal/g}$$

$$\Delta H_f^{298K}(\text{liquid}) = -16 \text{ kcal/mole} = -109 \text{ cal/g}$$

$$\Delta H_f^{298K}(\text{solid}) = -27 \text{ kcal/mole} = -183 \text{ cal/g}$$

$$\Delta H_{\text{vaporiz}} = 15 \text{ kcal/mole}$$

$$\Delta H_{\text{sublim}} = 26 \text{ kcal/mole}$$

It should be noted that the heats of formation for all three phases are negative. For comparison purposes, the solid phase heats of formation of HMX and RDX are, respectively, 60.4 cal/g and 76.1 cal/g [5].

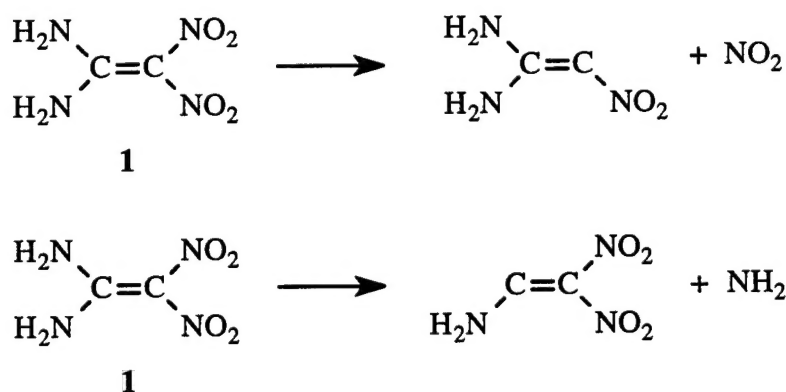
#### Specific impulse:

The specific impulse of **1** was estimated using the Newpep program (Naval Weapons Center, China Lake, CA) and also a program that we have written [6]. Our calculated solid phase heat of formation was used as input data in both instances. The predicted specific impulse, relative to that of HMX, is:

Newpep:        0.93                      Our program:        0.94

#### C-NO<sub>2</sub> and C-NH<sub>2</sub> Bond Strengths:

The strengths of the C-NO<sub>2</sub> and C-NH<sub>2</sub> bonds in **1** were determined by computing their dissociation energies, i.e.  $\Delta H(298 \text{ K})$  for the processes,



The geometries of **1** and the various products were optimized with the density functional B3P86/6-31+G\*\* procedure [7], and the resulting energies were converted to enthalpies at 298 K using the calculated vibration frequencies [8].

The results are:

C-NO<sub>2</sub> dissociation energy, (H<sub>2</sub>N)<sub>2</sub>C=C(NO<sub>2</sub>)<sub>2</sub>:     $\Delta H(298 \text{ K}) = 70.0 \text{ kcal/mole}$   
 C-NH<sub>2</sub> dissociation energy, (H<sub>2</sub>N)<sub>2</sub>C=C(NO<sub>2</sub>)<sub>2</sub>:     $\Delta H(298 \text{ K}) = 111.6 \text{ kcal/mole}$

For comparison, the dissociation energies of the C-NO<sub>2</sub> and C-NH<sub>2</sub> bonds in H<sub>3</sub>C-NO<sub>2</sub> and H<sub>3</sub>C-NH<sub>2</sub>, computed by the same procedure, are given below, together with the experimental values.

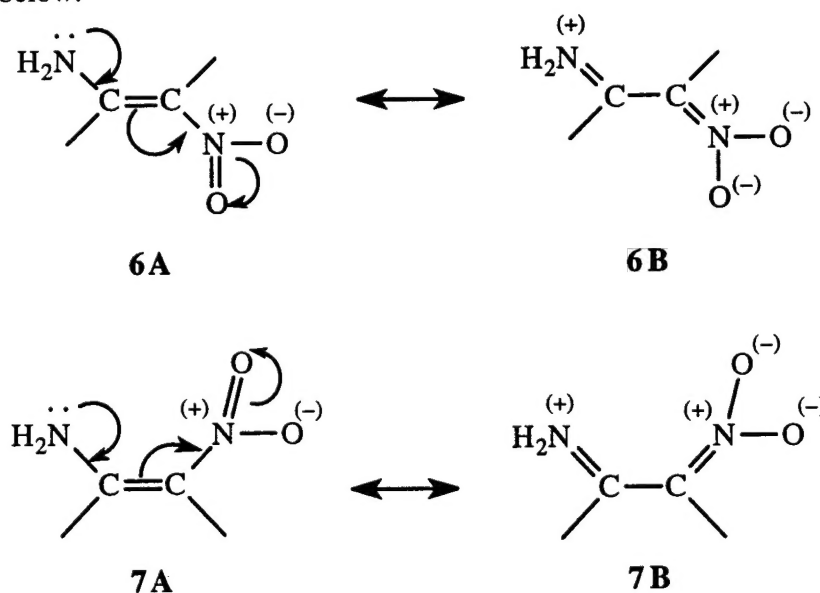
C-NO <sub>2</sub> dissociation energy, H <sub>3</sub> C-NO <sub>2</sub> [9]:	59.8 kcal/mole
Experimental [10]:	60.8 kcal/mole
C-NH <sub>2</sub> dissociation energy, H <sub>3</sub> C-NH <sub>2</sub> [9]:	84.6 kcal/mole
Experimental [11]:	84.9 kcal/mole

Thus the C-NO<sub>2</sub> and C-NH<sub>2</sub> bonds in **1** are stronger than in more typical cases such as H<sub>3</sub>C-NO<sub>2</sub> and H<sub>3</sub>C-NH<sub>2</sub>.

### Geometries:

In Figure 1 are presented the optimized geometries and corresponding energetic data, including relative enthalpies at 298 K, for **1** and for its isomers **2** and **3**. All calculations were at the density functional B3P86/6-31+G\*\* level.

The most stable of these molecules is **1**, with **2** and **3** being higher in enthalpy at 298 K by 4 and 17 kcal/mole, respectively. Among the factors that determine these relative stabilities are (a) the possibilities for intramolecular hydrogen bonding, and (b) delocalization of electrons, as shown in the examples below.



### (a) Intramolecular Hydrogen Bonding:

In Figure 1, the possible hydrogen bonds (which are primarily O---H in nature) are shown by dashed lines. There are two in **1**, and they can be considered to be relatively strong [12-14], with O---H distances of 1.77 Å. There are four in **2**, but they are not as strong, with O---H separations of about 1.90 Å and 2.08 Å. **3** also has four hydrogen bonds, one being N---H in nature, but they involve considerably greater distances and hence are relatively weak.

(b) *Electron Delocalization:*

The electron delocalization depicted above (sometimes termed "push-pull") reflects the combined effects of donation by the amine group and withdrawal by the nitro group, with the latter enhancing the former. Structures **6B** and **7B** suggest that the extent to which this is occurring can be gauged by the shortening of the C–NH<sub>2</sub> and C–NO<sub>2</sub> bonds and the lengthening of the C=C. In order to permit such comparisons, Figure 1 includes the computed geometries of **4** and **5**, in which the combined effect is precluded.

Examination of the respective bond lengths shows that the degree of electron delocalization is greatest in **1** and least in **3**. In the latter, the effect of one of the NH<sub>2</sub>, NO<sub>2</sub> pairs is quite similar to those in **2**; however the other NH<sub>2</sub>, NO<sub>2</sub> pair is not interacting in this fashion, as can be seen from the rotated and pyramidal nature of the NH<sub>2</sub> (which permits additional hydrogen bonding).

Comments:

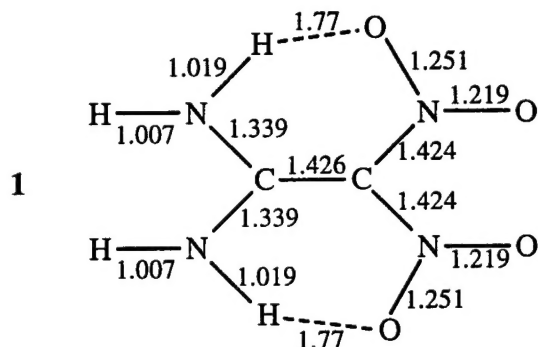
The analysis of molecular geometries has shown that **1** is significantly stabilized by both intramolecular hydrogen bonding and electron delocalization, to a greater extent than either **2** or **3**. Since both of these factors are diminished by removal of either an NO<sub>2</sub> or an NH<sub>2</sub> group, it follows that they should have the effect of increasing the C–NO<sub>2</sub> and C–NH<sub>2</sub> dissociation energies, as we have indeed found to be the case. In view of the widely-held belief that rupture of the C–NO<sub>2</sub> bond is a critical step in the decomposition processes of many energetic molecules [15-24], it can be anticipated that the greater strengths of these bonds in **1** will decrease its impact and shock sensitivities. On the other hand, the anomalous stability of **1** is responsible for its negative heats of formation.

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Figure 1. B3P86/6-31+G\*\* optimized geometries<sup>a</sup> and energies.<sup>b</sup>

$E = -599.70979$  hartrees

ZPE = 58.23 kcal/mole

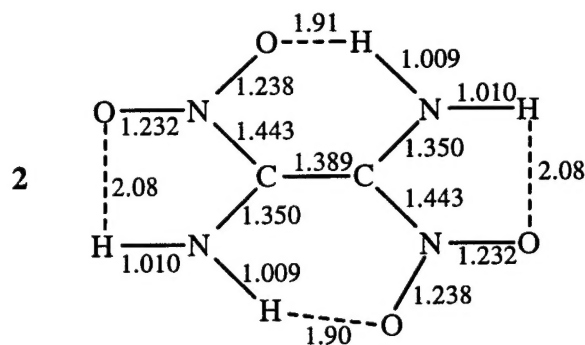
$\Delta H(0 \rightarrow 298) = 64.58$  kcal/mole

**Relative H(298 K) = 0**

Sums of carbon bond angles =  $360^\circ$

Sums of nitro bond angles =  $360^\circ$

Sums of amine bond angles =  $358^\circ$



$E = -599.70209$  hartrees

ZPE = 57.59 kcal/mole

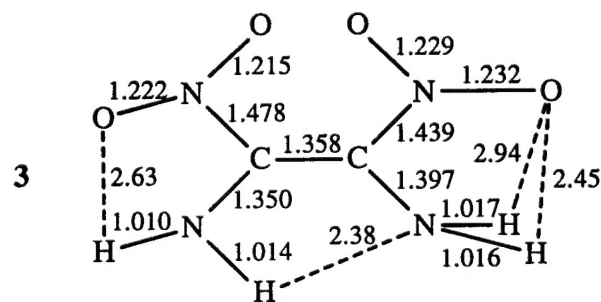
$\Delta H(0 \rightarrow 298) = 64.08$  kcal/mole

**Relative H(298 K) = 4.3 kcal/mole**

Sums of carbon bond angles =  $360^\circ$

Sums of nitro bond angles =  $360^\circ$

Sums of amine bond angles =  $357^\circ, 358^\circ$



$E = -599.68278$  hartrees

ZPE = 58.07 kcal/mole

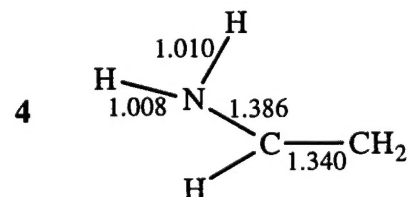
$\Delta H(0 \rightarrow 298) = 64.80$  kcal/mole

**Relative H(298 K) = 17.2 kcal/mole**

Sums of carbon bond angles =  $360^\circ$

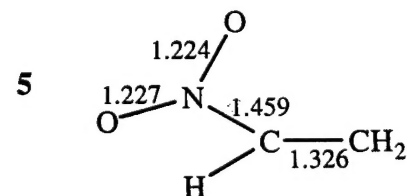
Sums of nitro bond angles =  $360^\circ$

Sums of amine bond angles =  $331^\circ, 350^\circ$



Sums of carbon bond angles =  $360^\circ$

Sums of amine bond angles =  $346^\circ$



Sums of carbon bond angles =  $360^\circ$

Sums of nitro bond angles =  $360^\circ$

<sup>a</sup>Distances are in Angstroms.

<sup>b</sup> $E$  = energy minimum at 0 K; it does not include the zero-point energy (ZPE).  $\Delta H(0 \rightarrow 298)$  is the enthalpy change in going from 0 K to 298 K; it includes the ZPE. Since  $E(0 \text{ K}) = H(0 \text{ K})$ , it follows that  $H(298 \text{ K}) = E(0 \text{ K}) + \Delta H(0 \rightarrow 298)$ .